



Short communication

Synthesis and electrochemical performance of layered lithium–sodium manganese oxide as a cathode material for lithium ion batteries



Ke Du^{a,c,*}, Kwang-Sun Ryu^{a,b,*}, Dianhua Huang^c, Guorong Hu^c

^a Energy Harvest-Storage Research Center, University of Ulsan, Daehak-ro 93, Nam-gu, Ulsan 680-749, Republic of Korea

^b Department of Chemistry, University of Ulsan, Daehak-ro 93, Nam-gu, Ulsan 680-749, Republic of Korea

^c School of Metallurgical Science and Engineering, Central South University, Changsha, PR China

HIGHLIGHTS

- $\text{Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2$ delivers an initial discharge capacity of 247 mAh g^{-1} in a lithium battery.
- $\text{Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2$ shows an initial average voltages of 3.52 V and energy density of 869 Wh kg^{-1} .
- $\text{Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2$ can be prepared by the classic solid state method with simple raw materials.

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ABSTRACT

$\text{Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2$ has been synthesized at different calcination temperatures by a solid state method. Its phase structure and electrochemical properties are investigated and discussed. $\text{Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2$ prepared at 600°C shows a complicated structure and wonderful electrochemical performance. In the voltage range of 2.0 and 4.8 V , $\text{Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2/\text{Li}$ cell delivers an initial discharge capacity of 247 mAh g^{-1} with an average voltage of 3.52 V , which demonstrates a very high energy density of 869 Wh kg^{-1} . Furthermore, the material displays a stable capacity greater than 240 mAh g^{-1} over 30 cycles.

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1. Introduction

Rechargeable lithium-ion batteries (LIBs) are considered the most promising energy storage technology for portable electronics, hybrid electric vehicles, and all-electric vehicles because of their high power and energy density [1–3]. A rechargeable LIB is typically composed of a cathode and an anode, which are electrically insulated by a porous polypropylene membrane in a nonaqueous electrolyte. Various cathode and anode materials have been investigated in past two decades [4,5]. Cathode was conventionally looked as lithium source and so the researched cathode materials are almost lithium-containing. However, Barker et al. introduced a

hybrid-ion battery and the non-lithium containing compound, NaVPO_4F , was used as the cathode material of lithium ion battery in 2004. The initial reversible capacity of the cathode was about 120 mAh g^{-1} [6]. And two other sodium phosphates, $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ [7–10] and $\text{Na}_2\text{FePO}_4\text{F}$ [11,12] were investigated later. The capacity of these phosphates is lower than 130 mAh g^{-1} . Though there are many published reports discussed the electrochemical performance of sodium salt of layered transition metal oxides in sodium ion batteries, their behavior in lithium ion batteries are barely researched. As far as we known, only Doeff studied $\text{Na}_{0.44}\text{MnO}_2$ and $\text{Na}_{0.2}\text{Li}_x\text{MnO}_2$ in polymer lithium battery that work at 85 or 105°C [13,14], though the initial capacity was about 180 mAh g^{-1} , the cycle stability is terrible.

Based on the idea that sodium ions can be electrochemically exchanged in lithium ion batteries, as shown in hybrid-ion battery, we investigated the electrochemical behavior of some sodium salts of layered transition metal oxides in lithium ion batteries. Among them, the manganese composite interested us most because of its

* Corresponding authors. Energy Harvest-Storage Research Center, University of Ulsan, Daehak-ro 93, Nam-gu, Ulsan 680-749, Republic of Korea. Tel.: +82 52 259 2763.

E-mail addresses: dukeben1976@yahoo.com, duke22@csu.edu.cn (K. Du), ryuks@ulsan.ac.kr (K.-S. Ryu).

high theoretic capacity, low cost, good safety and non-toxicity. A series of $\text{Na}_{1-x}\text{Li}_x\text{MnO}_2$ were synthesized and we found a certain component, $\text{Na}_{0.75}\text{Li}_{0.25}\text{MnO}_{2+\delta}$ (we prefer to write it as $\text{Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2$), shows a different structure with orthorhombic phase o- LiMnO_2 or monoclinic phase m- LiMnO_2 . It is similar to P2 structured $\text{Na}_{2/3}[\text{Li}_{1/6}\text{Mn}_{5/6}]\text{O}_2$ that reported by Paulsen et al. [15].

In this paper, we reported the synthesis of $\text{Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2$, a new layered lithium–sodium manganese oxide material, and investigated its electrochemical properties as a cathode in a lithium cell for the first time.

2. Experimental

Stoichiometric amount of Mn_2O_3 (Aldrich, 99.99%), Na_2CO_3 (Aldrich, 99.0%) and Li_2CO_3 (Fisher, 99.9%) were thoroughly mixed and then calcinated at high temperature for 24 h to obtain the desired products. The heating and cooling rates of the powder were 4 and 2 °C min⁻¹, respectively.

Charge–discharge tests were performed using coin type cells (CR2032). Each cell consisted of a positive electrode, which contained 80% active material, and a lithium metal negative electrode separated by a porous polypropylene film. The electrolyte solution was 1 M LiPF_6 in an ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:2 volume ratio) mixture. The cells were cycled galvanostatically at room temperature using a Maccor battery testing system.

To investigate the evolution of ion exchange, the elemental contents of the positive electrode at different stages were investigated. The cells were opened in a glove box and the positive electrodes were washed several times with DMC. After drying, the electrode material was carefully scraped and analyzed by X-ray diffractometry (XRD) and inductively coupled plasma optical emission spectrometry (ICP-OES).

The manganese oxidation state was determined as follows: a known amount of sample was dissolved under a flow of argon in dilute sulfuric acid containing a known excess of Fe^{2+} . Oxidation equivalents were determined by back titration with 0.01 M KMnO_4 .

Cyclic-voltammetry (CV) measurements were carried out by using Model 2273A Electrochemical Instruments (PerkinElmer Co., USA) at room temperature. The sweeping rate was fixed at 0.05 mV s⁻¹ in the voltage region of 2–5 V.

3. Results and discussion

Fig. 1 shows X-ray diffraction patterns of $\text{Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2$ sintered at 500, 600, 700, 800 and 900 °C. The five patterns can be divided into two groups. Patterns of 800 and 900 °C can be indexed as a structure with the most symmetric hexagonal space group $P6_3/mmc$. It is same as $\text{Na}_{2/3}[\text{Li}_{1/6}\text{Mn}_{5/6}]\text{O}_2$ reported in Ref. [15], proving that the P2 structure was achieved [16]. The hkl indices have been marked on the pattern of 900 °C sample. However, the patterns of 500, 600 and 700 °C show obvious difference. Several broad peaks centered at 46°, 53° and 57° are found, which maybe caused by stacking faults or impurity. Superstructure peaks are observed between 20 and 30°, which can be attributed to superlattice ordering of Li and Mn in the transition metal containing layers.

Fig. 2 shows the initial charge and discharge curves at a rate of 0.1 C for $\text{Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2$ prepared at five different temperatures. The three low temperature samples, 500, 600 and 700 °C, display initial charge curves with a plateau at ~4.7 V. The reaction mechanism of the material is similar to that of Li_2MnO_3 -based materials and the initial charge plateau is due to the simultaneous extraction of both Li and O from the materials [17,18]. The valence of Mn in $\text{Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2$ prepared at 600 °C was +4.02, which was determined by the titration method.

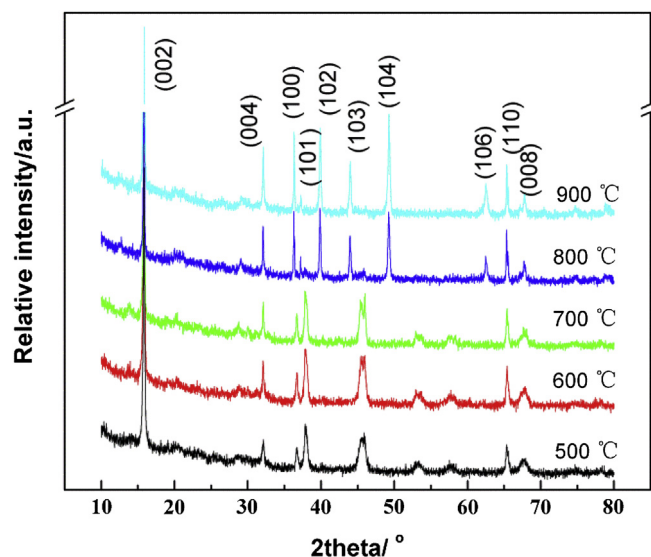


Fig. 1. XRD patterns of the $\text{Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2$ prepared at different temperatures. (The hkl indices of $\text{Na}_{0.7}\text{MnO}_{2+x}$ are shown).

In the initial discharge profiles of 500, 600 and 700 °C samples, a small plateau appears around 4.5 V and the voltage descends slowly from 4.5 to 2.8 V followed by a steep decrease between 2.8 and 2 V. The average voltages are 3.31, 3.52 and 3.40 V for these three discharge curves, respectively. The sample prepared at 600 °C shows the highest initial capacity of 247 mAh g⁻¹ and energy density of 869 Wh kg⁻¹. The value of energy density is almost 50% higher than that of LiCoO_2 . Therefore, this material can be used in Li-ion batteries that require high energy density. At the same time, compared to O2 structured $\text{Li}_{2/3}[\text{Li}_{1/6}\text{Mn}_{5/6}]\text{O}_2$ which has a reversible capacity in the range of 150 mAh g⁻¹ if cycled between 2 and 4.8 V [15], $\text{Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2$ prepared at 600 °C shows much higher capacity.

The initial charge and discharge curves are very different for 800 and 900 °C samples. The charge plateau decreases to about 4.5 V and is shorter than that of the low temperature sample. The discharge curve composed of two plateaus at 4.3 and 2.7 V, which is similar to the discharge characteristics of spinel LiMn_2O_4 . The capacities of these two high temperature samples are smaller than

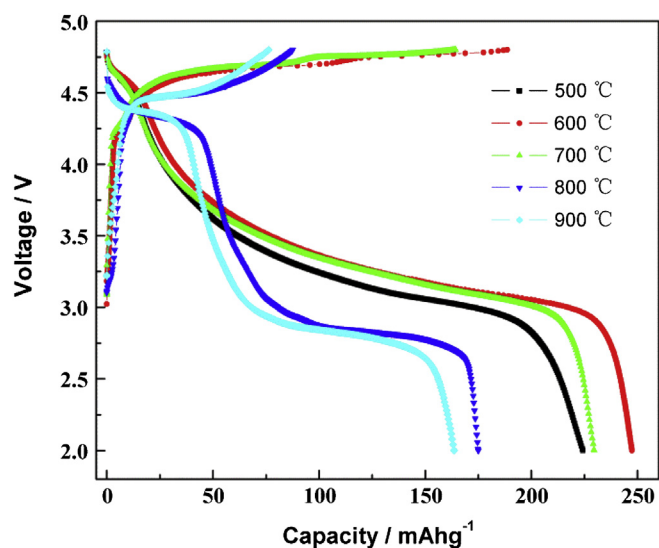


Fig. 2. The initial charge and discharge curves of the $\text{Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2$ prepared at different temperatures.

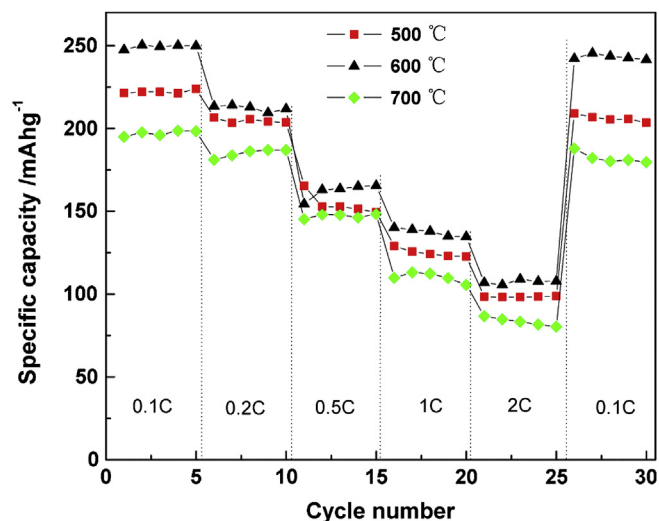


Fig. 3. The cyclic performance at different C-rates of the Na_{0.6}[Li_{0.2}Mn_{0.8}]O₂ prepared at 500, 600 and 700 °C.

those of low temperature samples. Obviously the difference of the electrochemical characteristic is caused by the structural difference.

The cycling stability of 500, 600 and 700 °C samples at different current rates were investigated and displayed in Fig. 3. The capacity significantly decreases with the increasing discharge rate and 600 °C sample delivers the highest capacity at each rate. Its capacity at 2 C rate is about 107 mAh g⁻¹. Although the rate performance is not satisfactory, its cycling stability is impressive: not only a small capacity fading is found at each rate, but also the capacity loss rate is small as the discharge rate returns to 0.1 C after 30 cycles at different rates. For example, the capacity of the 30th cycle for 600 °C sample is 242 mAh g⁻¹.

For understanding the outstanding capacity stability of Na_{0.6}[Li_{0.2}Mn_{0.8}]O₂ prepared at 600 °C, its evaluation of charge and discharge curves were studied and shown in Fig. 4. It can be found that the second charge curve, which features plateaus at 3 and 4.5 V, differs from the first charge curve. The charge capacity also increases to 280 mAh g⁻¹. The second discharge curve is smooth

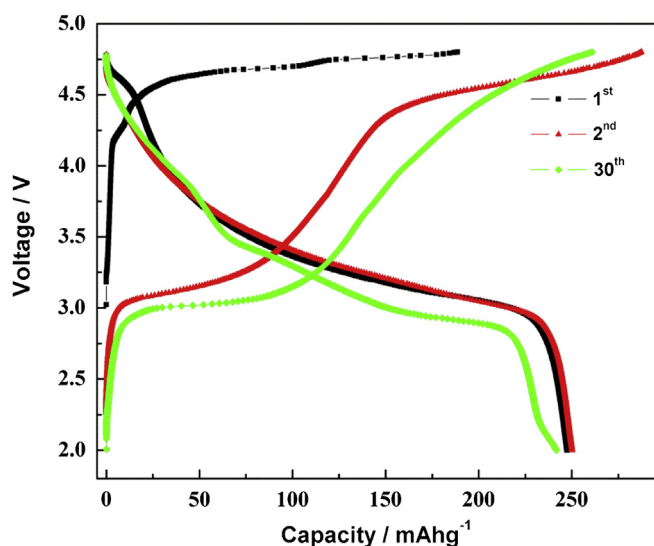


Fig. 4. The 1st, 2nd, and 30th charge and discharge curves of the Na_{0.6}[Li_{0.2}Mn_{0.8}]O₂ electrode prepared at 600 °C.

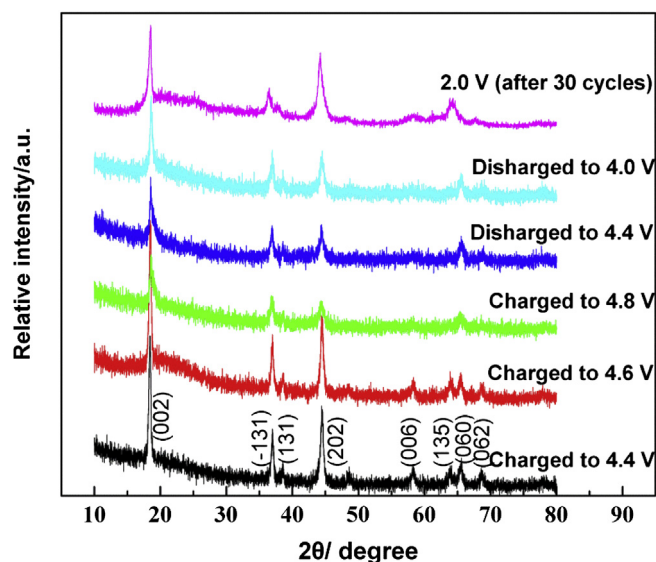


Fig. 5. Evolution of the XRD patterns of Na_{0.6}[Li_{0.2}Mn_{0.8}]O₂ electrode. (The *hkl* indices of Li₂MnO₃ are shown).

and very similar to the first one, but without the small 4.5 V plateau, and has a capacity of 250 mAh g⁻¹. After thirty cycles, there are some obvious changes: in the charge and discharge curves, the 4.5 V plateau disappears and the length of the 3 V plateau increases leading to an almost unchanged total capacity; the discharge curve becomes rougher and some small and inconspicuous plateaus appear in the curve suggesting structural changes occur during cycling.

To investigate the structure change of Na_{0.6}[Li_{0.2}Mn_{0.8}]O₂ during the charge and discharge process, *ex-situ* XRD patterns at different stages were investigated and displayed in Fig. 5. Three charged states (4.4, 4.6 and 4.8 V) and two discharged states (4.4 and 4.0 V) of the first cycle, and the full discharged state of the 30th cycle are compared. All the XRD patterns are similar to each other, but different from that of the as-prepared material. A new phase forms that can be indexed as Li₂MnO₃ (JCPDS: 27-1252); this means that the original structure of Na_{0.6}[Li_{0.2}Mn_{0.8}]O₂ is not stable toward the electrochemical charge process and quickly converts to a structure similar to that of Li₂MnO₃. Although Li₂MnO₃ itself is not a stable

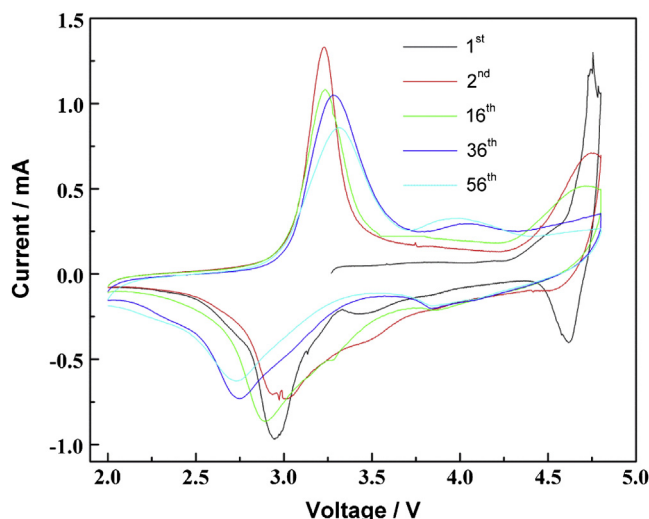


Fig. 6. Cyclic voltammograms of the Na_{0.6}[Li_{0.2}Mn_{0.8}]O₂ electrode prepared at 600 °C.

Table 1
Element ratios in the samples as-prepared and after different cycles.

	Li/Mn	Na/Mn	Na/Li
As-prepared	0.23	0.74	3.2
After 30 cycles	1.540	0.348	0.22
After 60 cycles	1.551	0.334	0.21

cathode material for lithium ion batteries as reported previously [19–21], the structure of this material is very stable during cycling over a wide voltage range. We believe that sodium plays an important role in this stability.

Cyclic voltammograms in the inset of Fig. 6 also disclose the change during the cycling. The initial CV of $\text{Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2$ prepared at 600 °C shows a strong oxidation peak at 4.75 V with a shoulder peak close to up the cut-off voltage of 4.8 V. Correspondingly, two reduction peaks are found at 4.61 and 2.95 V. For the second cycle, a large oxide peak at 3.25 V appears and the strength for the redox pair of 4.75/4.61 V become weak quickly. With the cycling, the redox pair of 4.75/4.61 V almost disappears in the curves of the 16th, 36th and 56th cycles and the polarization of the redox pair of 3.25/2.95 V increases. At the same time, a new pair of redox peaks at 4.05/3.84 V appears slowly. The results of CV are in good accordance with the charge and discharge curves.

The electrochemical exchange of sodium and lithium in $\text{Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2$ (600 °C)/Li cells were studied by comparing the ratio of Na/Li in the positive electrode after cycling and the result was listed in Table 1. It is found that Na/Li of the as-prepared sample is 3.2, a little larger than the expected value. Only after one charge–discharge cycle, the ratio of Na/Li decreases quickly to 0.26. In the following cycles, the ratio decreases slowly to 0.22 at the 30th cycle and 0.21 at the 60th, which indicates that a part of sodium is difficult to be exchanged electrochemically.

According to above charge–discharge data, *ex-situ* XRD and variation of component elements, we speculate that the initial $\text{Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2$ changes to a material with a component close to $\text{Li}_{2-x}\text{Na}_x\text{MnO}_3$ after electrochemical cycling. The lithiated phase is $\text{Li}_{2-x}\text{Na}_x\text{MnO}_3$ and de-lithiated phase is $\text{Li}_{1-x}\text{Na}_x\text{MnO}_3$. The *x* value varies with cycles and goes near a fixed value (~ 0.2).

4. Conclusions

In this paper, a new cathode material for lithium ion batteries, $\text{Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2$, was synthesized by a simple solid state method.

The sample prepared at 600 °C shows a high initial capacity of 247 mAh g^{−1} and an average voltage of 3.52 V, which corresponds to an energy density of 869 Wh kg^{−1} at the rate of 0.1 C. The cycling stability of $\text{Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2$ prepared at 600 °C is excellent with 242 mAh g^{−1} after 30 cycles. The synthesized $\text{Na}_{0.6}[\text{Li}_{0.2}\text{Mn}_{0.8}]\text{O}_2$ exchanges sodium with lithium from the electrolyte and the structure of the material also changes to Li_2MnO_3 type. The characteristics of charge–discharge curves and CV reflect the structure change. This new material is attractive for demanding Li-ion battery applications.

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